Computational Thermodynamics and Kinetics in Materials Modelling and Simulations

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Over the past two decades, Computational Thermodynamics and Kinetics have been tremendously contributed to materials modeling and simulations [1-5], and the demands on quantitative conceptual design and processing of various advanced materials arisen from various industries and academic institutions involved in materials manufacturing, engineering and applications are still rapidly increasing.

Through a sophistic combination of thermodynamic/kinetic models, computation techniques, databases and application programming interfaces, it is possible to predict material compositions, structures and properties resulted from various material processes. There have been several types of approaches involving computational thermodynamics and kinetics, which prove to be very successful in modelling and simulations of various materials: CALPHAD (Computer Coupling of Phase Diagrams and Thermochemistry), first-principles calculations (*e.g., ab initio*, DFT-Density Function Theory), MD (Molecular-Dynamics simulations), MC (Monte-Carlo simulations), Phase-Field simulations, CFD (Computational Fluid Dynamics), FEM/FDM (Finite Element Methods & Finite Difference Methods), among others.

The extended CALPHAD approach aims to promote Computational Thermodynamics and Kinetics to improve understanding of various industrial and technological processes in materials modeling and simulations, through the MSDI developments:

Models [representing thermodynamic properties and kinetic parameters for various phases/systems/processes] that permit predictions of phase equilibria, phase properties and phase transformations of multicomponent systems;

Software [for thermodynamic calculations (*e.g.*, Thermo-Calc, FACTSage, MTDATA, GEMINI, HSC, Pandat and JMatPro) and for kinetic simulations (*e.g.*, DICTRA, MICRESS and PrecipiCalc)] that can be used to optimize and derive thermodynamic properties and kinetic parameters, and perform various thermodynamic calculations and kinetic simulations that are required in materials designs and processing;

Databases [of thermodynamic properties and kinetic parameters] that are self-consistent and contain critically-assessed data based on available experimental measurements (of various thermochemical and phase equilibrium data, as well as of phase transformation information), empirical/semi-empirical equations and theoretical results (such as first-principles calculations); *and*

Interfaces [for application programming] that allow plugging the thermodynamic calculation and kinetic simulation engines into user-own application programs or third-party software packages, for more advanced or more specific calculations/simulations.

The SGTE (Scientific Group Thermodata Europe) organization has been significantly contributing to the developments and applications of the CALPHAD approach since 1979. Associated with some software available within the CALPHAD community, several high-quality databases have been developed by SGTE and its members through various international/national research projects, and by some other related organizations.

The Thermo-Calc/DICTRA software, database and programming interface packages [5-11] have been developed over the past 35 years, aimed at providing materials scientists and engineers with comprehensive assisting tools in their daily work of materials design and processing. This presentation will primarily focus on these two packages as the leading tools in the field of Computational Thermodynamics and Kinetics, and their applications in materials modelling and simulations.

Thermo-Calc is one of the most common software in the field of Computational Thermodynamics, which can calculate complicated heterogeneous phase equilibria and multi-component phase/property diagrams for many different types of materials. DICTRA is one of a few software currently available that can precisely simulate diffusion-controlled phase transformation in multicomponent metallic systems. DICTRA uses Thermo-Calc as its engine for all kinds of thermodynamic calculations, but extends to applications with complex kinetic problems engaged. They are most renowned worldwide for their powerful functionality, unique facilities, user-friendliness and wide applications, as well as for their flexible application programming interfaces (*i.e.*, TQ and TCAPI), easy-to-use toolboxes and links built in third-party software packages (*e.g.*, TC-Toolbox in MATLAB, and TC/DICTRA-Engine in MICRESS, PrecipiCalc, Hybrill and CAMDS), and complete GUI-driven graphical interfaces (*i.e.*, TCW). Furthermore, the PARROT module available in the Thermo-Calc/DICTRA software can be utilized for critical assessments and database developments.

Both software systems have been connected with many high-quality and internally-consistent thermodynamic and kinetic databases. At present moment, a wide spectrum of Thermo-Calc and DICTRA databases are available for various steels/Fe-alloys, Ni-based superalloys, Ti-/Al-/Mg-/Cu-/Zn-/Zr-based alloys, solder alloys, metal powders, ceramics, fuel-cell materials, slag, semi-/super-conductors, noble metals, minerals, nuclear materials, molten salts, aqueous solution, organic materials, and so on.

With the Thermo-Calc software and various thermodynamic databases, one can achieve, among others,

Phase diagrams (binary, ternary, isothermal, isoplethal, *etc.*) for systems with up to 5 independent variables;

Thermodynamic properties of pure substances, compounds and solution phases;

Thermodynamic properties of chemical reactions;

Contributions from magnetic ordering, chemical ordering, surface tension, electrostatic state, *etc.*;

Thermodynamic and transport properties of aqueous solutions over a wide *T-P-X* range (incl. critical region);

Property diagrams (G, H, S, V, C_p, C_v, μ, α, X, *etc.*) for systems with up to 40 components;

Heterogeneous interactions and partition coefficients for systems with up to 40 components;

Pourbaix diagrams and many other diagrams for aqueous-involving interaction systems;

Ellingham diagrams, Boudouard diagrams, potential diagrams, partial gaseous pressures (fugacities), *etc.*;

Scheil-Gulliver simulations of solidification and heat evolution for alloys with back diffusions of interstitials;

Liquidus surfaces, "γ-volume", and primary solidus projections for multicomponent alloys;

CVD diagrams, thin-film formation;

CVM calculations on chemical ordering-disordering phenomena;

Oxide-layer formation on steel surfaces, steel/alloy refining, so-called PRE numbers;

Speciation in corrosion, recycling, remelting, sintering, incineration, combustion;

Evolution of hydrothermal, metamorphic, volcanic, sedimentary, weathering processes;

Simulations of Carnot cycles, glass transitions;

Meta-stable equilibria, para-equilibria;

Special quantities: *e.g.*, T_o, A_3-temperature, adiabatic T, chill factors, $\partial T/\partial X$, *etc.;*

Thermodynamic factors and driving forces which

are important quantities for dynamic process simulations;

Simulations of steady-state reactors or dynamic reactors;

Critical assessments of experimental data, and establishment and modification of thermodynamic databases.

The DICTRA software and mobility databases, coupled with the Thermo-Calc software and thermodynamic databases, has been applied to solve several problems of scientific and practical interest, such as:

Solidification and microsegregation in steels;

Gradient sintering of cemented carbides;

Coarsening of γ'-precipitates in nickel base alloys;

Carburization and decarburization of steels;

Carburization of High-Temperature alloys;

Nitriding and Nitrocarburizing of steels;

Austenite/ferrite diffusional transformations in steels;

Calculation of CCT and TTT diagrams;

Interdiffusion in coating/substrate compounds;

Growth of pearlite in alloyed steels;

Microstructures of alloys;

Partitionless transformations under para-equilibrium;

Calculations of various diffusion coefficients (*e.g.*, tracer-, self-, intrinsic- and interdiffusivities);

Critical assessments of experimental data, and establishment and modification of mobility databases.

Using the TQ/TCAPI programming interfaces and

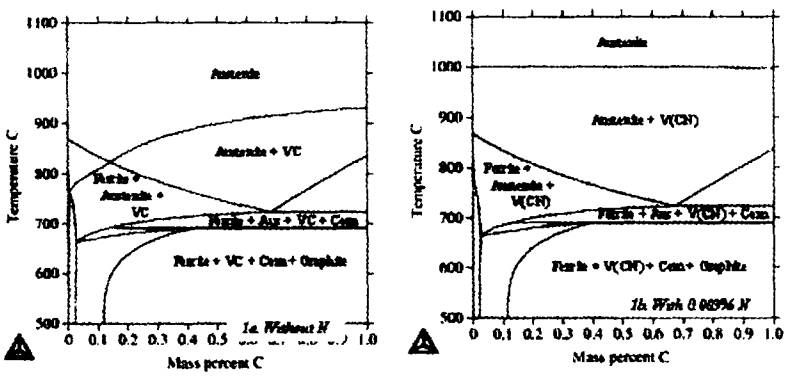

Fig. 1. Thermo-Calc Calculation Example: Isopleths for a HSLA steel, exploring how a small addition of nitrogen can change phase diagram and change the properties of material. Alloy content is Fe-1.5Mn-0.3Si-0.1V-C (in wt%). V(C,N) particles act as grain refiners

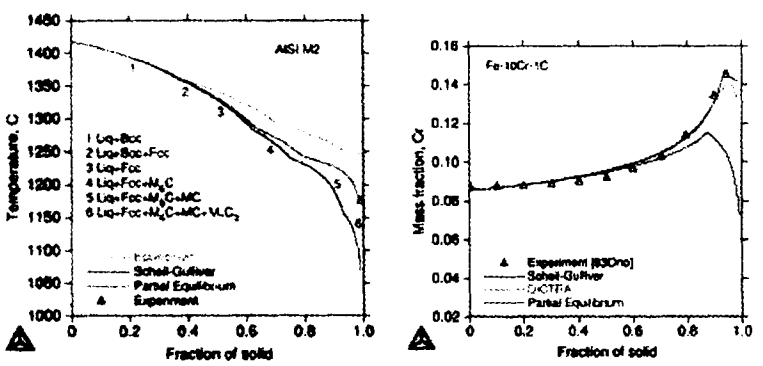

Fig. 2. Thermo-Calc Calculation Example: Simulation of solidification paths and microsegressions for two Fe-based alloys with bulk compositions of Fe-0.3Co-3.9Cr-0.1Cu-0.32Mn-4.9Mo-0.36Ni-0.3Si-6.1W-1.9V-0.88C and Fe-10Cr-1C (wt%), respectively

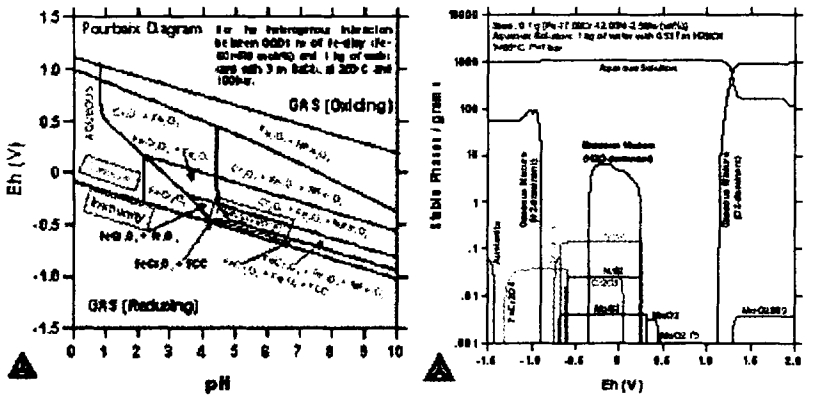

Fig. 3. Thermo-Calc Calculation Example: Pourbaix diagrams and property diagrams for heterogeneous interaction systems between 0.001 m of steel [Fe-5Cr-5Ni mole%] and 1 kg of water (and with 3 m NaCl), at 200oC and 100 bar), and between 0.1 g of steel [Fe-17.00Cr-12.00Ni-2.5Mo (wt%)] and 1 kg of water (and with 0.537 m H2SO4, at 85oC and 1 bar), respectively

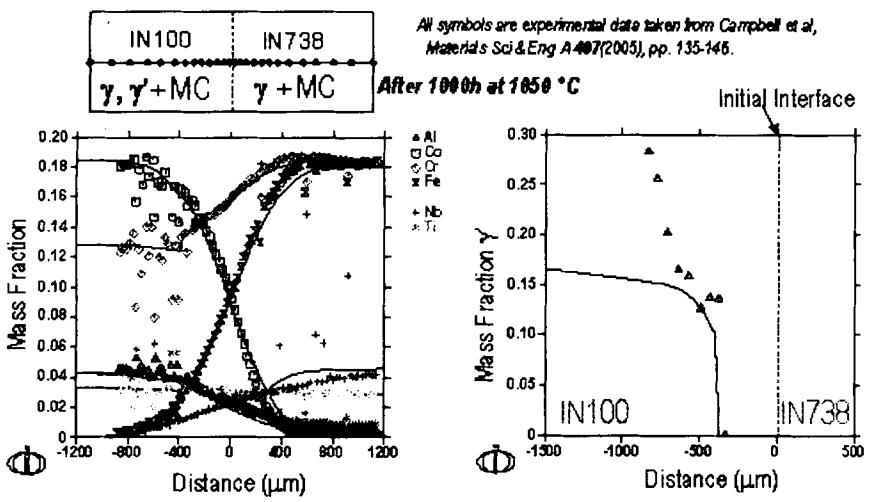

Fig. 4. DICTRA Simulation Example: Simulation of inter-diffusion phenomena in a complex diffusion couple between IN100 and IN738 alloys

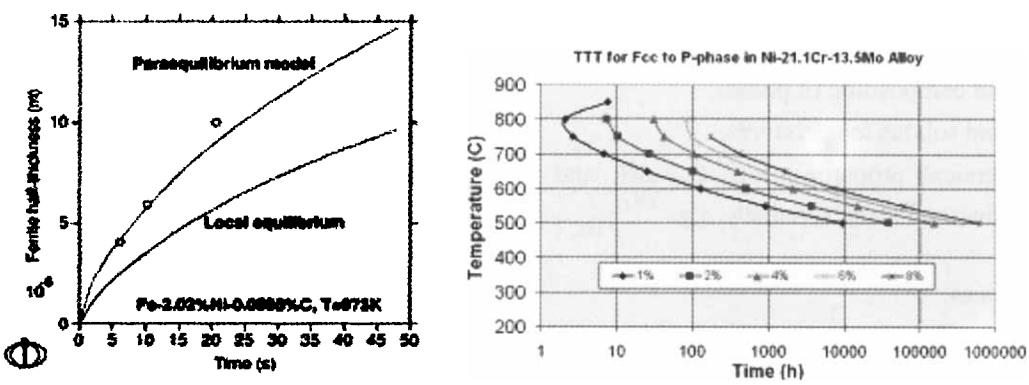

Fig. 5. DICTRA Simulation Example: Simulations of growth of ferrite into austenite in an Fe-2.02%Ni-0.0885%C alloy at 973 K (Result for local equilibrium at phase interface is compared with paraequilibrium assumption and recent experimental data), and of TTT diagram for FCC→P-phase transformation in an Ni-21.1%Cr-13.5%Mo alloy

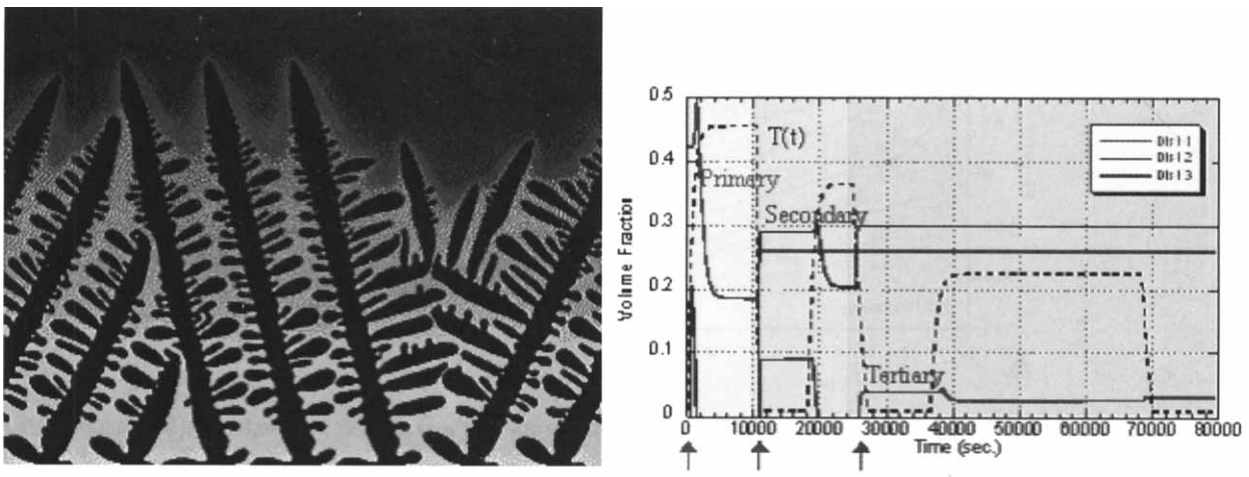

Fig. 6. Programming Interfaces - Application Example: Simulations of dendrite formation (growth of primary and secondary dendrites), using MICRESS™ software (developed by ACCESS) which interfaces with TQ; and of precipitation in a Ni-based superalloy under a complex commercial heat treatment, using PrecipiCalc™ software (developed by QuesTek Innovations) which interfaces with TCAPI

TC-Toolbox in MATLAB, most of the quantities that are available from Thermo-Calc (and to some extents from DICTRA) can be obtained, *e.g.*, temperature, pressure, volume, chemical potential, phase amount, phase composition, partition coefficients, liquidus or solidus points, invariant temperature, heat of reaction, adiabatic combustion temperature and diffusion coefficients (when used in conjunction with a suitable mobility database). Furthermore, they can be applied not only to equilibrium calculations but can also be used to predict metastable or non-equilibrium states by changing the status of the phases under consideration. Examples of quantities and properties that can be calculated using the programming interfaces are, among others:

Amount and composition of phases;

Liquidus and solidus temperatures;

Thermochemical properties, *e.g.* C_p, ΔH; and various derivatives of state variables, *e.g.* $\partial G_m^o / \partial x_i$, $\partial^2 G_m^o / \partial x_i \partial x_j$;

Driving forces;

Diffusion coefficients;

Partition coefficients;

Invariant temperatures;

Thermodynamic limits for partitionless transformations under para-equilibrium and quasi-paraconditions.

Such packages have been applied world-widely in steel/alloys-making and metallurgical industries, specific-alloy design and engineering, chemical engineering, hydrometallurgy, powder-metallurgy, materials applications (in *e.g.*, car and automotive industries, heavy industries, telecommunication industries, precise-equipment industries, aeronautic and astronautic industries, defense industries, petroleum industries, polymer industries, food industries, *etc.*), energy conversions and utility, earth materials, geochemical and natural-resource exploitations, nuclear power-plant safety and nuclear waster-repository assessments, aqueous chemistry, materials corrosion, environmental protections, and so forth.

The great capacities in calculating material properties, predicting material structures and simulating material processes have been demonstrated by many successful applications of the Thermo-Calc/DICTRA software, database and programming interface packages in industrial and academic R&D activities [1-24]. Some proven examples of using these software, databases and programming interfaces for enhancements in materials design and processing (especially in advanced steels/alloys

research and development) will be shown in this presentation. Fig. 1 — Fig.6 illustrate a few such examples.

Also be given will be some discussions on the further development of the Thermo-Calc/DICTRA software, database and programming interface packages in the near future.

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